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(54) Application of fluorochemicals to textile substrates.

(57) A method for treating fibrous textile substrate is presented comprising the steps of:
a) applying, as a mist, onto the substrate, an aqueous liquid composition comprising from 0.2 to 2 % by weight of a fluorochemical substance or substances, wherein the number median diameter of the droplets in said spray is from 20 to 70 microns, and wherein said application is such that a uniform application of from 0.2 to 1.5 weight % of solids based on the weight of the substrate is deposited onto said substrate, and
b) heating the resulting treated substrate at temperatures of from 85°C to 116°C sufficient to remove substantially all of the water from the applied aqueous liquid and to cure or coalesce the applied fluorochemical substance or substances.

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This invention relates to methods of treating textiles, by applying thereto, as a fine spray or mist, fluorochemical compositions.

In the industrial production of textiles, e.g., fibers and fabrics, it is common to treat the surface of the textile with a composition to impart added desirable surface properties thereto, such as oil and water repellency and resistance to soiling. Fluorochemical compositions are commercially used for this purpose and various patents and publications disclose a variety of such compositions.

Methods of generating sprays or mists by atomization of bulk liquids are well-known. See, for example, the methods described in "Atomization", Encyclopedia of Science & Technology, pp 214 to 218, McGraw-Hill, Inc., (1987). The word "misting" is often applied to the production of fine drops of 10 to 100 microns.

Currently, good performance is achieved by spraying organic-solvent based compositions onto textiles. Aqueous treatment compositions are sometimes spray applied and allowed to air-dry at ambient temperature, but larger amounts of solids on fabric, e.g. 1.5 weight % or greater, are needed to obtain desired repellency. The typical airless sprayers used in these applications produce aqueous sprays with an average droplet size of about 80 to 110 microns or higher. Some aqueous compositions are dried or cured at elevated temperatures, e.g. 310 °F (154 °C), to obtain improved performance. However, many fabrics, such as olefins or acrylics, are temperature-sensitive, that is they may be damaged by exposure to such temperatures.

Briefly, in one aspect, the present invention provides a method for treating a fibrous textile substrate, e.g. an olefin or acrylic fabric, to impart water and oil repellency thereto, comprising the steps of:

a) applying, as a mist, onto the substrate, an aqueous liquid composition comprising fluorochemical surface-modifying, substance or substances, e.g. fluorochemical adipate ester; and

b) heating the resulting treated substrate at moderate elevated temperatures sufficient to coalesce or cure said fluorochemical substance or substances and to remove substantially all of the water from the applied aqueous liquid composition;

and wherein the concentration of said substance or substances in said liquid composition, the droplet size of said mist, and the amount of substance applied to said substrate being such that water and oil repellency is efficiently imparted to the treated substrate.

The method of this invention can be used to achieve the performance levels of organic solvent systems without the use of volatile organic solvents. Conventional methods using aqueous treatment compositions only achieve the performance results of the present invention with higher heating or at higher, and therefore less economical, % of treatment solids on fabric. The method of this invention can be used to treat heat-sensitive fabrics such as olefins and acrylics to achieve desired repellency at economical levels of treatment chemical.

The aqueous liquid compositions useful in this invention are aqueous liquid compositions which are preferably substantially free of volatile organic solvents. The fluorochemical substances dissolved or dispersed in the aqueous media are preferably present in from 0.2 to 2 % solids by weight of the total aqueous composition. If the composition is too dilute, then it may be necessary to apply more of the composition to the substrate and it may take too long to dry the water from the substrate. If the composition is too concentrated, the resulting repellency performance is not as desirable as when less concentrated compositions are used.

The fluorochemical substances contained in the aqueous treatment mixtures are preferably those that will soften or flow at temperatures around 240 °F (116 °C) or below. Examples of useful fluorochemical substances are those described in U.S. Pat. No. 4,264,484 (Patel) which discloses a liquid carpet treating composition containing a water-insoluble addition polymer derived from polymerizable ethylenically unsaturated monomer free of nonvinylic fluorine and having at least one major transition temperature higher than about 24 °C and a water-insoluble fluoroaliphatic radical- and aliphatic chlorine-containing ester having at least one major transition temperature higher than about 25 °C.

Further examples of useful fluorochemical substances are those described in U.S. Pat. No. 4,401,780 (Steel) which discloses fluorochemical compositions which comprise a mixture of a) water-insoluble fluoroaliphatic radical- and aliphatic chlorine-containing ester; b) water- insoluble fluoroaliphatic radical-containing polymer; and c) water-insoluble fluoroaliphatic radical-containing compound selected from carbonylimino compounds and imine compounds.

Particularly preferred treatment compositions are those which contain, either alone or in combination with other substances, a fluoroaliphatic radical-containing ester derived from a fluoroaliphatic radical-containing alcohol and a carboxylic acid of 5 to 11 carbon atoms. Particularly preferred esters are those derived from adipic acid, citric acid, or phthalic acid.

Spray application which results in an average droplet size of from 20 to 70 microns may be used in the method of this invention.

Aerosol sprays can produce mists and therefore can be used in the method of this invention. Aerosols however, generally cannot readily be used to treat large areas, and therefore are generally not used in the production of treated textiles.

Commonly used spray guns where the treating solution is delivered from a reservoir and forced into an air stream through a nozzle, the force of the air causing the atomization of the liquid. These guns may be used if the spray is adjusted to give suitably fine spray or mist. The spray droplets are carried to the textile substrate by the air stream. This system is commonly used for applying paints, varnishes, oils, etc. but is not found in the general treatment of textiles in production due to the complexities of controlling the resulting overspray.

High-pressure airless-sprayers, usually electrical spray-guns capable of developing pressures behind the medium being sprayed of 900-1100 pound per square inch gauge are also useful. These guns function by the oscillating action of a piston and do not require pressurized air to function. When used with small orifices, they produce extremely fine particles of spray medium.

Other spray systems which may be used to give fine sprays or mists include, for example, electrostatic spraying which involves adding an electrical charge to the spray gun, and adding the opposite electrical charge to the substrate. This results in a uniform application. Electrostatic spraying can be utilized in both airless and atomization spraying systems. In another method of generating spray, a spray is generated by impinging a liquid stream onto a rotating disk.

When used to treat textiles, for example spraying at room temperature onto a moving textile web comprising textiles, such as those described in Table 1 on page 763 Kirk-Othmer, "Encyclopedia of Chemical Technology", Vol. 22, 3rd ed., John Wiley & Sons (1983), the method of this invention is preferable used to apply from 0.2 to 1.5 weight % solids based on weight of the fabric ("% SOF"), more preferably from 0.2 to 0.6 % SOF, and most preferably 0.4 to 0.6 % SOF.

In the method of this invention, the treated substrate is preferably heated to between 185 °F (85 °C) to 240 °F (116 °C). Such heating can be performed in one or more heating steps, for example heating first to dry and then heating at a slightly higher, but still at 240 °F (116 °C) or lower, temperature to cause the fluorochemical substance to cure or coalesce.

EXAMPLES

In the following Examples and Comparative Examples, textile samples were treated by mist or spray application of various fluorochemical compositions. The oil and water repellency of the resulting treated fabrics were evaluated.

Oil Repellency Test Method

The oil repellency of treated fabrics is measured by AATCC Standard Test 118-1978, which test is based on the resistance of treated fabric to penetration by oils of varying surface tensions. Treated fabrics resistant only to "Nujol", a brand of mineral oil, and the least penetrating of the test oils, are given a rating of 1, whereas treated fabrics resistant to heptane, the most penetrating of the test oils, are given a value of 8. Other intermediate values are determined by use of other pure oils or mixtures of oils. The rated oil repellency corresponds to the most penetrating oil (or mixture of oils) which does not penetrate or wet the fabric after 30 seconds contact. In some cases, ratings in one-half point increments were assigned where slight wetting of the fabric occurred but no penetration was observed. Higher numbers indicate better oil repellency. In general, an oil repellency of 4 or greater is desirable.

The oil repellency of tested fabrics after abrasion is measured by abrading 5 cm x 12.5 cm samples of fabric (the long dimension is the warp direction) using 40 back-and-forth rubs over a 20 second period with No. 600 abrasive paper (WETORDRY TRI-M-ITE", commercially available from 3M Co.) in an AATCC crockmeter. The above described AATCC oil repellency Test 118-1978 is performed on the abraded samples and the oil repellency rating recorded. In general, an oil repellency after abrasion of 3 or greater is desirable.

Water Repellency Test Method

The aqueous repellency of treated samples is measured using a water/isopropyl alcohol test, and is expressed in terms of the WATER/IPA" rating of the treated fabric. Treated fabrics which are penetrated by or resistant only to a 100% water/0% isopropyl alcohol mixture, the least penetrating of the test mixtures, are given a rating of 100/0, whereas treated fabrics resistant to a 0% water/100% isopropyl alcohol mixture,

the most penetrating of the test mixtures, are given a rating of 0/100. Other intermediate values ar determined by use of other water/isopropyl alcohol mixtures, in which the percentage amounts of wat r and isopropyl alcohol are each multiples of 10. The WATER/IPA rating corresponds to the most penetrating mixture which does not penetrate or wet the fabric after 15 seconds contact. In general, a WATER/IPA rating of <50/>50 is desirable.

Particle or Droplet Size Measurement

Droplet size was determined using a lazer diffraction particle sizer. See, e.g. "Dynamic Plume-Particle Size Analysis Using Lazer Diffraction", Pharmaceutical Technology, pp 108 to 114, (October 1992). Droplet size was measured using a Malvern™ 2600C, with a 100mm lens, operated in a model independent mode to give a number-average drop-diameter.

Example 1

An aqueous treatment composition was prepared as follows. A polyurethane was prepared by adding to a 2-L three-necked flask equipped with a mechanical stirrer, thermometer, reflux condenser, nitrogen inlet tube, and heating mantle, 1062 g N-methyl perfluorooctanesulfonamidoethyl alcohol and 708 g ethyl acetate. After heating with stirring to about 55 C under nitrogen atmosphere, a premixed solution of 616 g of DesmodurTM N-100 isocyanate available from Mobay Co. and 300 g ethyl acetate are added. Then, 0.84 g stannous octoate was added and the reaction mixture was stirred at about 75 °C for 6 hours. A premixed solution of 1044 g CarbowaxTM 1450 available from Union Carbide and 807 g ethyl acetate was added. The resulting mixture was stirred and heated at reflux at about 83°C for 16 hours. Substantially all of the isocyanate functionality had been converted at this time as indicated by infrared spectroscopy.

To a 2-L three-necked flask equipped with an overhead stirrer, a thermometer, and a reflux condenser were added 184.6 g of the above polyurethane, 178.7 g of a) $C_8F_{17}SO_2N(CH_3)C_2H_4OCOCH=CH_2$, b) $CH_2=C(CH_3)COO(CH_2O)_{90}H$, c) $CH_2=C(CH_3)COO(CH_2CH_2O)_{90}COC(CH_3)=CH_2$, in a 1:1 weight ratio of a:(b+c) and a 3:1 weight ratio of b:c prepared as generally described in U.S. Pat. No. 3,787,351 (Example) at 47% solids in ethyl acetate, 36 g of adipate ester prepared as described in U.S. Pat. No. 4,264,484 (Example 8), 125 g ethyl acetate, and 960 g of deionized water. The resulting mixture was vigorously stirred for 60 minutes while being heated to 60 to 70 C. The solvent was removed by vacuum stripping to give a 20% solids, stable dispersion which was diluted with water to 1% solid and then used as an aqueous treatment composition.

The above aqueous treatment composition was sprayed onto an olefin velvet fabric (100% olefin woven upholstery, pattern rows, color: Maron 05014 from Joan Fabrics Corp. Lowell, MA) using the following atomized spray technique.

The atomized spray system consisted of a Model 6000 hand sprayer, equipped with a No. 40100 nozzle and a No. 120SS spray cap manufactured by Spraying Systems Co., hereafter referred to as a "MISTER" sprayer. The gun was hand held while spraying a weighed piece of fabric supported on a tared balance. Spraying was continued until the calculated, desired weight to give 50% pickup by weight was achieved. Spraying was carried out uniformly by moving the spray back and fourth and up and down across the sample. Air pressure on the gun during spraying was maintained at 40 p.s.i.g., and the gun was held approximately 12 inches above the sample. The average particle size in the mist was measured to be from 27 to 23 microns. The resulting solids on fabric (SOF) was 0.5%.

Following spraying, the sprayed fabric was dried in an air circulating oven for 10 minutes at 125°F. then cured or annealed separately at 220°F. for 5 minutes while supported on a pin frame to prevent the fabric from contacting the hot interior surfaces of the oven. Following curing, or annealing, the fabric sample was conditioned at least 4 hours at 72°F. before testing.

The conditioned, treated fabrics were tested for oil repellency (identified under the columns entitled Repellency and is identified as OR), Water Repellency (identified as WR) and Oil Repellency after Abrasion (identified as OR-ABR). The results are shown in Table 1.

Example 2

A second 1% solid aqueous emulsion treatment composition was prepared as described in U.S. Pat. No. 4,401,780 (Example 12), which mixture contains the adipate ester described in U.S. Pat. No. 4,264,484 (Example 8).

As in Example 1, except with the second aqueous treatment composition, the aqueous composition was sprayed onto the same type of olefin velvet fabric. Drying, curing or annealing, and testing was done as described in Example 1. Test results are shown in Table 1.

Comparative Example C1

The aqueous treatment composition of Example 1 was applied using conventional airless spraying onto the same type of olefin velvet fabric as in Example 1.

In the conventional airless spraying, the sample was transported under a bank of spray nozzles (Spraying System nozzles #SS11001) on a variable speed conveyor. The nozzles were mounted across the area traversed by the conveyer so that adjacent nozzles overlapped their spray patterns to give double coverage of the treatment composition to the substrate. Air pressure employed on the system while spraying was 60 p.s.i.g., and the conveyor speed was adjusted to give 50% pickup for each fabric, i.e. 0.5 % SOF. Average drop diameter in the spray was from 80 to 110 microns. Drying, curing or annealing, and testing was done as described in Example 1. Test results are shown in Table 1.

Comparative Example C2

The aqueous treatment composition used in Example 2 was used as described in Example 2 except the conventional airless sprayer of Comparative Example C1 was used instead of the atomized spray system of Example 1. Test results are shown in Table 1.

TABLE 1

	OR	WR	OR-ABR
Example 1	5.0	7.0	5.0
Example 2	4.0	6.0	6.0
Comp. Ex. C1	1.0	FAIL	0.5
Comp. Ex. C2	1.5	2.0	4.5

The data show that conventional airless spraying of Comparative Example C1 and C2 when followed by low temperature curing conditions of 220°F did not produce repellency as good as that achieved with the atomized sprayer used in Examples 1 and 2. The atomized spray system of Example 1 and 2 did produce fabrics with good repellency, even on difficult to treat olefin velvet.

Examples 3 and 4

Example 3 and 4 were made and tested as in Examples 1 and 2 respectively, except an Acrylic Velvet (Dralon, pattern 1237, color buff 312 from La France Inds., La France, SC.) was used instead of the olefin velvet fabric. The results are shown in Table 2.

Comparative Examples C3 and C4

Comparative Examples C3 and C4 were made and tested as in Comparative Examples C1 and C2 respectively, except the Acrylic Velvet fabric of Examples 3 and 4 was used instead of the olefin velvet fabric. The results are shown in Table 2.

TABLE 2

	OR	WR	OR-ABR
Example 3	5.0	9.0	4.0
Example 4	5.0	7.0	5.0
Comp. Ex. C3	1.0	FAIL	1.0
Comp. Ex. C4	2.0	1.0	4.0

The data show that the conventional airless spraying of Comparative Example C3 and C4 do not giv repellency on acrylic velvet as good as the atomized spray used in Examples 3 and 4.

Exampl 5

Example 5 was prepared and tested as in Example 1 except the applied amount was increased to 1.5 % SOF. The results are shown in Table 3.

Comparative Example C5

Comparative Example C5 was prepared and tested as in Example 5 except the treated sample was allowed to dry at room temperature overnight instead of the 125° F drying step and 220° F cure or anneal step. The results are shown in Table 3.

Comparative Example C6

Comparative Example C6 was prepared and tested as in Example 5 except the conventional airless sprayer of Comparative Example C1 was used instead of the atomized spray system of Example 1. The results are shown in Table 3.

Comparative Example C7

Comparative Example C7 was prepared and tested as in Comparative Example 2 except the applied amount was increased to 1.0% solids on fabric. The results are shown in Table 3.

TABLE 3

	OR	WR	OR-ABR
Example 5	5	8.0	6.0
Comp. Ex. C5	5	8.5	6.0
Comp. Ex. C6	2.0	FAIL	6.0
Comp. Ex. C7	1.5	1.0	6.0

The data in Table 3 illustrate that even high levels of application do not give good performance unless applied by the atomized spray system of this invention.

Example 6

Example 6 used a Nylon Flat Weave of 100% Nylon Flat upholstery, ready for printing, scoured and backed from Chatham Manufacturing Co., Elkin, NC.. Example 6 was prepared and tested as in Example 1 except using this fabric and the SOF level was 0.3%. The results are shown in Table 4.

Comparative Examples C8 and C9

Comparative Example C8 and C9 were prepared as in Comparative Example C1 except the SOF level was 0.3 % for C8 and 1.5 % for C9. The fabric treated was the same as that used in Example 6. The Comparative Examples were tested as in Example 1, the results are shown in Table 4.

TABLE 4

	OR	WR	OR-ABR
Example 6	6.0	8.0	6.0
Comp. Ex. C8	4.0	FAIL	4.0
Comp. Ex. C9	5.0	1.0	5.0

The data in Table 4 show that when sprayed with conventional airless spraying, the nylon upholstery did not have repellency as good as when the treatment composition was applied with the "MISTER" sprayer.

Examples 7 to 9 and Comparative Examples C10 to C12

The following Examples and Comparative Examples were prepared as in Example 1. The SOF level was 0.3 % and the aqueous treatment compositions used were as follows: Example 7 used the aqueous treatment mixture of Example 1; Example 8 used the aqueous treatment mixture of Example 2; Example 9 used was a 1% aqueous emulsion comprising an about 50 to 50 mixture of an acylate polymer prepared as in U.S. Pat. No. 4,043,964 (Example II) except with a 95 to 5 weight ratio of 95 to fluoroalphatic acrylate to butylacrylate and a polyurethane prepared as described in U.S. Pat. No. 3,398,182 using components labeled therein as fluorocarbon compound V, hydrocarbon compound LI, and reactive compound PAPI 27 isocyanate.

TABLE 5

	OR	WR	OR-ABR
Example 7	4.5	7.5	2.0
Example 8	4.0	5.0	4.0
Example 9	3.0	6.0	2.0

Examples 10 to 14

The following Examples were made and tested as in Example 1. The substrates were various fabrics as shown in Table 6. The results are shown in Table 6.

Comparative Examples C10 to C14

The Comparative Examples C10-C14 were prepared as in Comparative Example C1 except using the fabrics shown in Table 6. The results are shown in Table 6.

In Table 6 the following abbreviations are used to designate the various fabric used in each Example and Comparative Example: "Cotton" is cotton sheeting - white, bleached, and mercerized, upholstery weight, style 409 from Testfabrics Inc. Middlesex, NJ; "Ole Vel" is the same fabric used in Example 1; "Ole Blend" is 48% olefin, 18% rayon, 34% polyester, flat, pattern 9352, Christie, color is Wedgewood from Chromatex, Rossville, GA; "Acr Vel" is the same fabric used in Example 3; and "Ny Flat Weave" is the same fabric used in Example 6.

TABLE 6

EXAMPLE	FABRIC	OR	WR	OR-ABR
10	Cotton	6.0	9.0	5.0
11	Ole Vel	4.0	8.0	4.0
12	Ole Blend	5.0	8.0	5.0
13	Acr Vel	5.0	9.0	4.0
14	Ny Flat Weave	6.0	10.0	6.0
C10	Cotton	2.0	3.0	FAIL
C11	Ole Vel	1.0	FAIL	FAIL
C12	Ole Blend	2.0	1.0	2.0
C13	Acr Vel	2.0	2.0	2.0
C14	Ny Flat Weave	5.0	2.0	5.0

The data in Table 6 show that significantly better repellency was obtained with the "MISTER" spray as described in the present invention, compared to conventional airless spraying. The data in Table 6 also

show that the invention is effective on a wide range of fabrics.

Comparative Examples C15 to C22

To compare the application of solvent-carried fluorochemicals using the process of this invention to the conventional airless spraying, samples of olefin velvet (Comparative Examples C15 to C18) and acrylic velvet (Comparative Examples C19 to C22) were sprayed in the laboratory using the hand held sprayer described as the "MISTER" and also by a specially equipped airless spray system equipped for solvents.

Airless solvent spraying was carried out on continuous equipment fitted with high ventilation, and two supply systems and two spray booms fitted with individual spray heads, one used only with aqueous systems, the other used only with solvent systems. A variable speed conveyor was used to transport the fabric under the spray heads. The nozzle used was Spraying Systems SS650050.

Handling of the fabric, drying, curing (or annealing), and testing was as described in Example 1. In each Comparative Example the % SOF was 1.5%. The results are shown in Table 7.

An organic solvent treatment composition was prepared as follows. A copolymer was prepared as described in U.S. Pat. No. 3,341,497 (Example VIII) except the fluorine-containing monomer was N-methyl perfluorootanesulfonamidoethylacrylate and the ratio of fluorocarbon monomer to acrylate comonomer was 65 to 35 weight %. A 25 % solids solution in ethyl acetate (25 % by volume) and heptane (75 % by volume) was further diluted with mineral spirits to about 11.6% solid for the olefin fabric and 13.9% solids for the acrylic fabric. When dry, this fluorochemical leaves a contiguous film.

TABLE 7

EXAMPLE NO.	SPRAY METHOD	OR	WR	OR-ABR
C15	AIRLESS	2.0	5.0	FAIL
C16	AIRLESS	3.0	6.5	FAIL
C17	MISTER	2.0	6.5	1.0
C18	MISTER	2.5	7.0	1.0
C19	AIRLESS	1.0	5.0	1.0
C20	AIRLESS	5.0	8.0	1.0
C21	MISTER	2.0	6.0	1.0
C22	MISTER	5.5	9.0	1.0

The data in Table 7 show that there is no significant difference in airless spraying and "MISTER" (atomized) spraying repellencies of solvent-carried fluorochemicals. The advantages of the invention of this invention are surprisingly only realized when spraying aqueous treatment compositions.

Examples 15 to 18

Examples 15 and 16 were prepared as in example 1 except the substrate was nylon type 6,6 carpet, and except that the aqueous treatment compositions used were those described below. The results are shown in Table 8.

Examples 17 and 18 were prepared and tested as in Examples 15 and 16 respectively except that the substrate was a nylon type 6 carpet instead of nylon type 6,6 carpet. The results are shown in Table 8.

Comparative Examples C23 to C26

Comparative Examples C23 and C24 were prepared and tested as in Examples 15 and 16 except the spray system utilized was that described in Comparative Example C1. The results are shown in Table 8.

Comparative examples C25 and C26 were prepared and tested as in Examples 17 and 18 except the spray system utilized was that described in Comparative Example C1. The results are shown in Table 8.

The aqueous treatment composition used in Examples 15 and 17 and in Comparative Examples C23 and C25 was a 1% solids aqueous emulsion prepared as described in U.S. Pat. No. 4,264,484 (Example 8).

The aqueous treatment composition used in Examples 16 and 18 and in Comparative Examples C24 and C26 was a 1% solids aqueous emulsion prepared as in U.S. Pat. No. 4,264,484 (Example 8) except the weight ratio of fluoroalphatic polymer to addition polymer was 2 to 1.

TABLE 8

EXAMPLE NO.	OR	WR
15	3.0	1.0
C23	1.0	FAIL
16	2.0	2.0
C24	1.0	FAIL
17	3.0	1.0
C23	2.0	FAIL
18	3.0	1.0
C26	2.0	1.0

The data in Table 8 show that better repellencies were obtained where the fluorochemicals were applied with the air atomized sprayer, than with the airless sprayer.

Examples 19 and 20

A 1% solids aqueous treatment composition was prepared containing two parts of Asahi GuardTM AG-480 (believed to contain fluorochemical telomer polymer) and one part of the adipate ester described in Example 1. This treatment composition was used in Examples 19 and 20 for treating olefin velvet and acrylic velvet respectively. Samples of each fabric were sprayed with the Mister to give 0.5 % SOF after drying at 125°F and curing at 220°F as in Example 1. The treated samples were tested as in Example 1. The results are shown in Table 9.

Comparative Examples C27 and C28

Comparative Examples C27 and C28 were prepared and tested as in Examples 19 and 20 except with the airless sprayer of Comparative Example C1 instead of the Mister sprayer. The results are shown in Table 9.

Comparative Examples C29 and C30

Comparative Examples C29 and C30 were prepared and tested as in Comparative Examples C27 and C28 except that the treatment composition did not comprise the adipate ester. The results are shown in Table 9.

Examples 21 and 22

Examples 21 and 22 were prepared and tested as in Examples 19 and 20 except that the treatment composition did not comprise the adipate ester. The results are shown in Table 9.

Table 9

SAMPLE NO.	FABRIC USED	SPRAY METH.	OR	WR	OR-ABR
C27	Acr Vel	AIRLESS	2.0	2.0	3.0
C28	Ole Vel	AIRLESS	1.0	2.0	5.0
19	Acr Vel	MISTER	4.0	6.0	4.0
20	Ole Vel	MISTER	4.0	6.0	6.0
C29	Acr Vel	AIRLESS	F	2.0	FAIL
C30	Ole Vel	AIRLESS	F	1.0	FAIL
21	Acr Vel	MISTER	4.5	5.5	1.0
22	Ole Vel	MISTER	2.0	3.0	FAIL

The data show that, as before, the method of this invention gives higher repellency performance that conventional application methods. The data also show that treatment compositions without adipate ester did

not give repellency as high as compositions which did contain adipate ester.

Examples 23 and 24

Examples 23 and 24 were prepared and tested as in Example 1 except that the treatment composition used was as in Example 1 except without the adipate ester. The fabric used is shown in Table 11. The results are shown in Table 11.

Comparative Examples C31 and C32

Comparative Examples C31 and C32 were prepared and tested as in Examples 23 and 24 except with the sprayer of Comparative Example C1. The results are shown in Table 11.

TABLE 11

Example NO.	FABRIC USED	SPRAY METH.	REPELLENCY		
			OIL	HOH	ABR
23	Ole Vel	MISTER	2.0	7.0	FAIL
24	Acr Vel	MISTER	3.0	8.0	FAIL
C31	Ole Vel	AIRLESS	FAIL	FAIL	FAIL
C32	Acr Vel	AIRLESS	1.0	1.0	FAIL

The data again show that higher repellency is obtained by the method of this invention then with conventional methods.

Example 25

Olefins velvet was treated and tested as in Example 1 except the aqueous treatment solution was an emulsion of the fluoroaliphatic-radical containing phthalic ester prepared as described in U.S. Patent No. 4,264,484 (Example 3) except using an equivalent amount of phthalic acid in place of citric acid. The results are shown in Table 12.

Example 26

Olefins velvet was treated and tested as in Example 1 except the aqueous treatment solution was an emulsion of the fluoroaliphatic-radical containing phthalic ester prepared as described in U.S. Patent No. 4,264,484 (Example 3).

Table 12

Example	OR	WR	OR-ABR
25	5.0	4.0	6.0
26	5.0	4.0	6.0

Examples 27 and 28

In Examples 27 and 28, olefin velvet was treated and tested as in Examples 1 and 2 respectively except the treatment solutions were applied with a Wagner™ Model 200 power sprayer with a 0.4 mm tip. The average droplet size in the mist was determined to be between 30 to 33 microns. The fabric samples were sprayed using a pressure of approximately 1100 pounds. The results are shown in Table 13.

Table 13

Example	OR	WR	OR-ABR
27	5.0	8.0	4.0
28	4.0	5.0	5.0

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

Claims

1. A method for treating fibrous textile substrate comprising the steps of:
   a) applying, as a mist, onto the substrate, an aqueous liquid composition comprising from 0.2 to 2 % by weight of a fluorochemical substance or substances, wherein the number median diameter of the droplets in said spray is from 20 to 70 microns, and wherein said application is such that a uniform application of from 0.2 to 1.5 weight % of solids based on the weight of the substrate is deposited onto said substrate, and
   b) heating the resulting treated substrate at temperatures of from 85 °C to 116 °C sufficient to remove substantially all of the water from the applied aqueous liquid and to cure or coalesce the applied fluorochemical substance or substances.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 11 6987

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
D,X	US-A-4 401 780 (STEEL) * examples 1-7 and corresponding notes under table I * * column 9, line 67 - column 10, line 36; claims; table 1 *	1	D06M15/277 D06M15/576 D06M23/10 D06M23/06
X	FR-A-1 169 799 (RUDOLPF KOEHLERT) * claims *	1	
A	EP-A-0 257 800 (FADEGUARD INC.) * claims *	1	
A	US-A-3 401 052 (THOMAS W. BERGER ET AL.) * claims *	1	
A	EP-A-0 252 576 (E.I. DU PONT DE NEMOURS AND COMPANY) * claims *	1	
A D	US-A-4 340 749 (KALYANJI U. PATEL) * claims; examples 6-10 * & US-A-4 264 484 (PATEL)	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)

D06M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19 January 1994	Blas, V

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
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L : document cited for other reasons

& : member of the same patent family, corresponding document

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